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A toolbox for parameter-free predictions of solid-state properties of monodisperse glassy polymers with frozen-in molecular orientation

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ABSTRACT

This study presents a toolbox for the prediction of birefringence and craze initiation stress in oriented monodisperse linear amorphous polymers. The toolbox is assembled from a previously proposed melt-solid constitutive model that provides the necessary residual stress components required for predictions of birefringence and craze initiation stress. The Likhtman-McLeish theory for linear rheology of entangled polymers is employed to generate the low reduced frequency part of the linear viscoelastic spectrum, the only molar mass dependent input parameter. All other parameters are obtained by experiment or from literature, and can be considered material constants. Toolbox predictions are compared to new experimental data on two grades of linear monodisperse polystyrene of known molar mass but unknown rheology and to literature data. The toolbox is able to account for the role of molar

mass on birefringence and craze initiation stress of polystyrenes subjected to supra-entanglement orientation processes.

KEYWORDS polystyrene, orientation, constitutive model, birefringence, crazing

INTRODUCTION

The flow processes that occur during melt-processing of polymers can result in varying degrees of frozen-in molecular orientation within polymer products in the solid-state. In some classes of products, such as oriented films and fibres, the orientation is intentional and desired. In other classes of products, such as injection mouldings and extrusions, it is an unintentional consequence of the competition between processes of shearing and relaxation during the flow of polymer melts. Frozen-in molecular orientation is frequently an important consideration of any design, since its presence leads to anisotropy of many material properties of practical interest. Such anisotropy has been readily observed experimentally through measurable changes of Young's modulus^{1,2}, yield stress³⁻⁶, crazing stress⁷⁻¹¹, optical birefringence^{1,3,8,12-14}, strain-hardening modulus^{4-6,15,16}, rate of ageing¹⁷ and fracture toughness¹⁸⁻

²¹.

Most of these properties are not only dependent on the direction of orientation, but are also highly sensitive to both the grade of polymer employed and to the flow history encountered during processing^{10,14,15}. Hence, irrespective of whether the orientation is desired or not, the design of polymeric products generally consists of three interconnected stages: (1) the selection of an appropriate type and grade of polymer; (2) the specification of processing parameters; and (3) the realisation of the

desired solid-state properties in the processed product. The authors have recently proposed a new, fully 3-dimensional constitutive model that employs the linear viscoelastic spectrum in the melt and solid states to predict the non-linear melt-state and solid-state constitutive response of glassy polymers¹⁵. By fitting this model to linear viscoelastic rheological data obtained from two monodisperse linear polystyrenes (PS), the authors demonstrated a remarkable result: that it is possible to predict the optical birefringence¹⁴, the craze initiation stress¹⁰, and the solid-state mechanical response²² of a polymer of given molar mass subjected to an arbitrary process history, with a small number of molar mass independent material constants and experimental measurement of the molar mass dependent melt-state linear viscoelastic spectrum.

For the special case of linear monodisperse polymers, however, the melt-state linear viscoelastic response can be predicted accurately through the use of Likhtman and Mcleish's quantitative physical theory for linear entangled polymer melts²³. The aim of this paper is to take the final step towards completely parameter-free property predictions of solid-state properties of processed polymers. Thus, whereas previously linear rheological experimental data for each polymer grade was employed to provide input to the conformational part of the relaxation spectrum, here this is obtained directly from theory. This critical step enables connectivity between theories whose input parameters are all material constants associated with a particular polymer species. The goal is to enable polymer product designers to make seamless connections between (1) the selected grade of polymer and (2) the defined process history in order to achieve (3) specific solid-state properties in the processed polymer, by provision of a toolbox of inter-connected theories requiring the minimum number of experiments and material constants.

First, new experimental measurements of birefringence and craze initiation stress are carried out on two monodisperse PS grades of significantly different molar mass subjected to a range of uniaxial melt orientation processes. This is followed by an outline of the essential elements of the constitutive model and of the theories for prediction of solid-state properties. Likhtman and Mcleish's quantitative linear theory²³ is used to predict the melt-state linear viscoelastic response, and process simulations are performed using parameters computed from this prediction. Outputs from these simulations are used to predict two solid-state properties of practical engineering interest: optical birefringence and craze initiation stress. Toolbox predictions are compared to the new experimental measurements and to literature data, and discussed.

EXPERIMENTAL

Materials

The materials used in this study were two samples of monodisperse linear atactic PS with $M_w = 121$ kDa (BE) and $M_w = 966$ kDa (BB) and narrow polydispersities ($PDI = M_w/M_n < 1.1$). Material BE was provided by Prof. Mackley of the University of Cambridge, and material BB was provided by Dr Lian Hutchings, synthesised by living anionic polymerization at the University of Durham. Molar mass measurements were performed relative to PS standards by size exclusion chromatography on a Viscotek TDA 302 machine and an Agilent Technologies PL-GPC 120 with refractive index, viscosity and light scattering detectors, and results are given in Table 1. Previously published experimental data from two further samples of monodisperse linear atactic PS with $M_w = 262$ kDa (AF) and $M_w = 518$ kDa (AG) and narrow polydispersities ($PDI = M_w/M_n < 1.15$) are also employed in this study and listed in Table 1¹⁵.

Table 1 Molar mass measurements obtained by triple detection SEC for polystyrene samples BE and BB used in this study, and for polystyrene samples AF and AG from reference ¹⁵.

Code	M_n (kDa)	M_w (kDa)	PDI (-)	Architecture	Source
BE	113.7	121.1	1.07	linear	this study
BB	900.8	966.4	1.07	linear	this study
AF	250.9	262.4	1.05	linear	ref. [15]
AG	449.1	517.6	1.15	linear	ref. [15]

Production of oriented specimens

The need to minimize waste polymer during moulding because of limited availability of monodisperse materials, as well as the need to minimise the stress applied to specimens during their removal from the mould, required the development and use of a near net shape moulding technique, described in detail elsewhere²⁴. Fresh sheets of disposable aluminium foil were used to line the upper and lower surfaces of the moulds in order to provide a repeatable surface texture on the moulded specimens. The mould components were lightly sprayed with a dry PTFE mould release aerosol, prior to each moulding operation. Each cavity of the mould was filled with a small excess of polymer before the mould was between pre-heated press platens. The polymer was held at the moulding temperature of 170 °C for a period of 10 minutes in order to ensure full relaxation of the polymer, prior to cooling at a rate of ~15 °C min⁻¹, as described previously¹⁵, and removal from the mould. With this technique, small numbers of optically isotropic parallelepipedic bars were produced with approximate dimensions of 80 mm × 6 mm × 0.5 mm.

Oriented specimens were produced by uniaxial melt-drawing the prismatic bars of PS in an Instron 5985 testing machine fitted with an environmental chamber, at a range of temperatures T above T_g between

105 °C and 135 °C. All stretching was carried out at a constant crosshead velocity corresponding to a nominal strain rate of 0.02 s^{-1} , to a fixed stretch ratio of $\lambda = 3$. Specimens were quenched using a cold spray as quickly as possible at the end of the experiment. The initial cooling rate was measured on a representative bar as $\sim 15 \text{ }^{\circ}\text{C s}^{-1}$. The oriented bars were unloaded and stored at room temperature prior to subsequent testing.

Birefringence

Retardation, r , was measured on the central region of all oriented specimens at room temperature using an Olympus BX51-P transmission optical polarizing microscope fitted with strain-free optics, polarizer, and a thick Berek ($0-20\lambda$) rotary compensator, under white light, following a previously described procedure¹⁴. Birefringence, Δn , was computed from measurements of retardation and specimen thickness t as $\Delta n = r / t$. Birefringence values are reported in Figure 1 as a function of draw temperature.

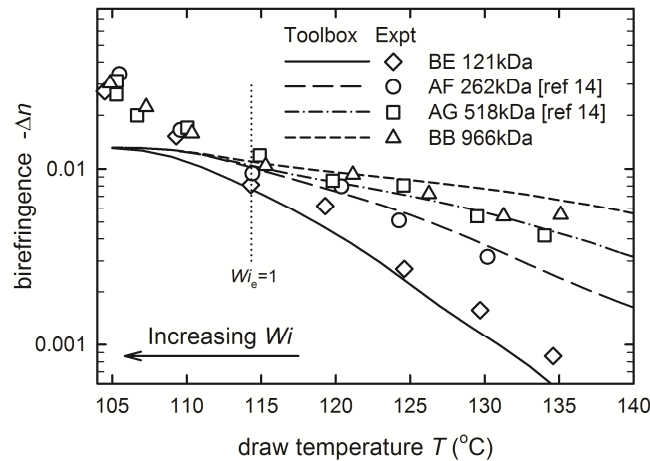


Figure 1 Experimental measurements of birefringence as a function of draw temperature for specimens of BE and BB drawn at a strain rate of 0.02 s^{-1} to a draw ratio of $\lambda = 3$ and immediately quenched (triangles and diamonds). Also shown are measurements of birefringence on two further grades of

monodisperse polystyrene AF and AG oriented under the same conditions from ref. ¹⁴ (circles and squares). Simulations of birefringence performed using the toolbox and constitutive model (lines).

Craze initiation stress

A previously described technique was employed for the measurement of craze initiation stress of miniature specimens subjected to isochronal 3-point bending creep, and only a brief account is given here²⁵. Miniature beams approximately 6 mm × 2 mm × 0.5 mm were cut from the oriented specimens using a custom jig. Specimens were soaked in reagent grade diethylene glycol for 24 hours prior to creep testing. The beams were loaded in 3-point bending creep for 300 s, with the beam axis (and hence the tensile stress) aligned with the direction of orientation, in the presence of diethylene glycol. After unloading, the dimensions of the crazed region were measured using optical microscopy, allowing the determination of the stress σ_c at which crazes have just initiated in the given time (referred to hereafter as the craze initiation stress). Miniature beams were also cut from isotropic moulded specimens and subjected to the same creep conditions in order to determine the isotropic crazing stress σ_c^{iso} . Measurements of the increase in crazing stress with orientation $\sigma_c - \sigma_c^{iso}$ are reported in Figure 2 as a function of draw temperature, as averages obtained from a minimum of four beams per experimental condition, and error bars represent two standard errors.

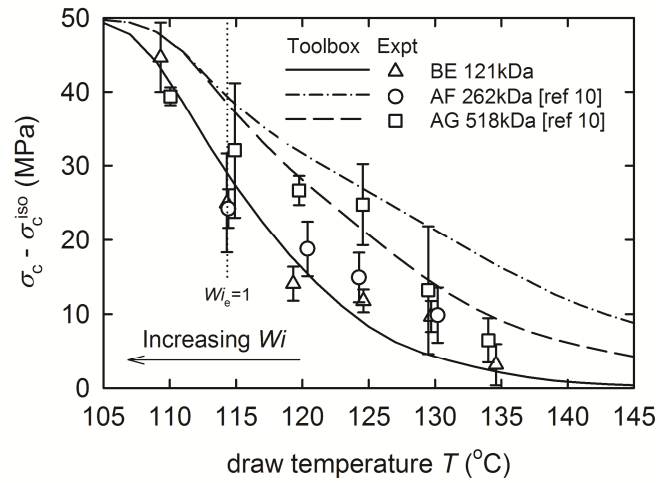


Figure 2 Measurements of the increase in craze initiation stress with orientation as a function of draw temperature for specimens of BE drawn at a strain rate of 0.02 s^{-1} to a draw ratio of $\lambda = 3$ and immediately quenched (triangles). Also shown are measurements of craze initiation stress on two further monodisperse polymers drawn under the same conditions from ref. ¹⁰ (circles, squares). Toolbox predictions of the increase in craze initiation stress with orientation performed using the toolbox and constitutive model (lines).

TOOLBOX

The objective of this work is to present a toolbox for the prediction of multiple solid-state properties of glassy polymers with process-induced molecular orientation. A schematic outline of the interdependence between material constants, elements of theory and predictions is provided in Figure 3 to aid the reader.

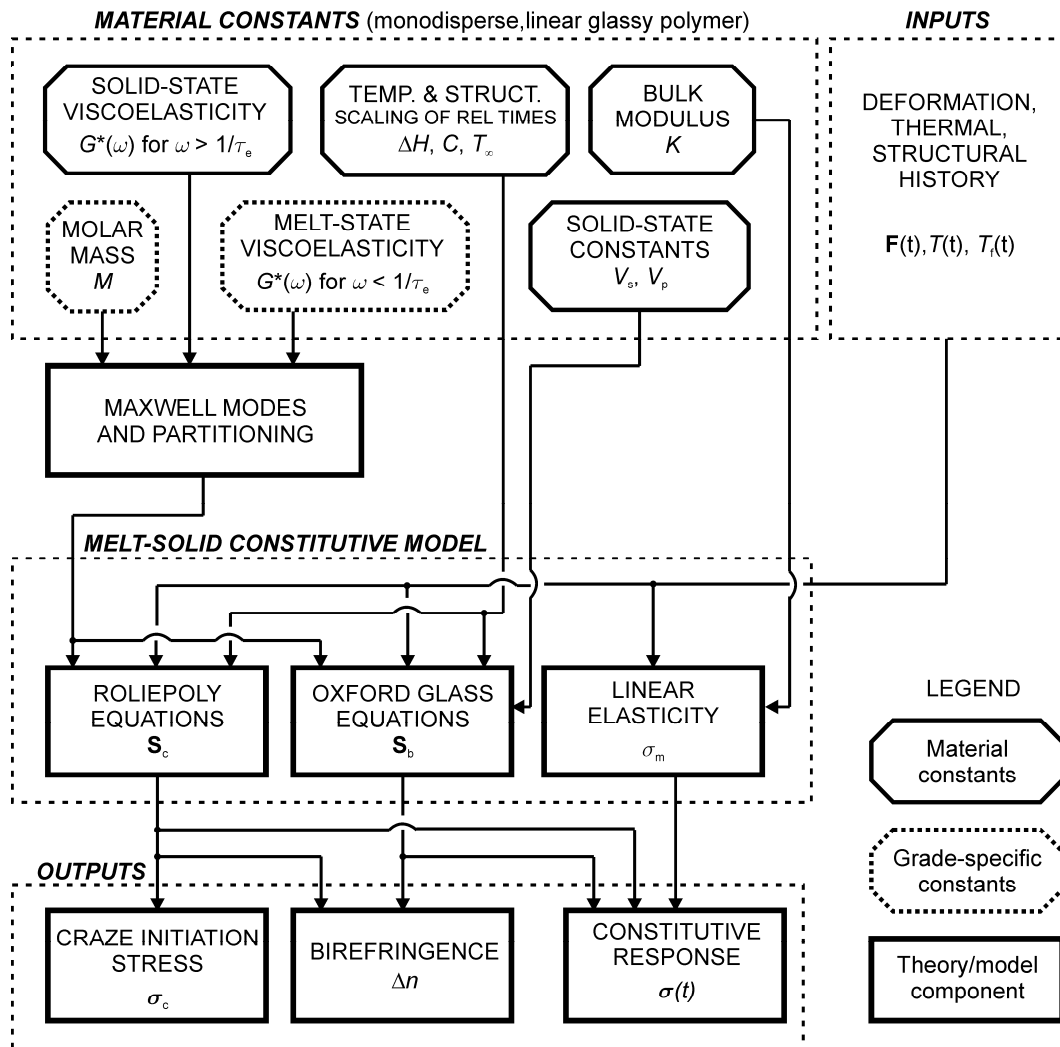


Figure 3. A schematic outline of the elements, inputs and outputs of the toolbox. The process of obtaining Maxwell modes and partitioning is shown in greater detail in Figure 4.

Melt-solid constitutive model

A fully 3-dimensional constitutive model for the melt-state and solid-state response of monodisperse polymer glasses was recently proposed by the present authors, suitable for the prediction of solid-state properties of oriented polymers. The model has been described in detail previously¹⁵, and only an

outline will be given here, with particular focus on the features which render it predictive from a molecular perspective.

The model describes the response of material to a deformation gradient tensor \mathbf{F} in terms of the Cauchy stress tensor $\boldsymbol{\sigma}$, separated into volumetric σ_m and deviatoric \mathbf{S} parts. The volumetric stress is given by $\sigma_m = \frac{1}{3}\text{trace}(\boldsymbol{\sigma}) = K \ln J$, where K is the bulk modulus and $J = \det \mathbf{F}$ is the volumetric part of \mathbf{F} . The deviatoric stress \mathbf{S} is expressed as the sum of bond-stretching \mathbf{S}_b and conformational \mathbf{S}_c contributions, $\mathbf{S} = \mathbf{S}_b + \mathbf{S}_c$, from the assumption of additivity of bond-stretching and conformational free energies.

In the bond-stretching part of the model, the deviatoric rate of deformation $\bar{\mathbf{D}} = \frac{1}{2}(\bar{\mathbf{L}} + \bar{\mathbf{L}}^T)$ is given by the sum of a linear elastic part and a viscous flow part

$$\bar{\mathbf{D}} = \frac{\hat{\mathbf{S}}_{b,j}}{2G_b} + \frac{\mathbf{S}_{b,j}}{2G_b\tau_j} \quad (1)$$

for each mode j of a spectrum of Maxwell modes, where $\bar{\mathbf{L}} = \dot{\mathbf{F}}\mathbf{F}^{-1}$ and $\dot{\mathbf{F}}$ is the time derivative of \mathbf{F} , $\hat{\mathbf{S}}_j^b$ is the Jaumann rate of stress, G_b is the bond-stretching shear modulus, and τ_j is the glassy relaxation time associated with the j th mode. The deviatoric stress is computed as the sum over all M bond-stretching modes, as $\mathbf{S}_b = \sum_{j=1}^M v_j \mathbf{S}_{b,j}$ where v_j represents the relative volume fraction of the j th glassy mode. The reader is referred to references²⁶⁻³⁰ for a more detailed discussion.

The conformational stress is computed from the Rolie-Poly constitutive model³¹, extended for finite extensibility of chains¹⁵. A conformational stress is computed for each Rolie-Poly mode k across a spectrum of N discrete Rolie-Poly modes by numerical integration of the differential equation describing the evolution of the orientation tensor \mathbf{T}_k . The orientation tensor evolves according to

$$\dot{\mathbf{T}}_k = \bar{\mathbf{L}} \cdot \mathbf{T}_k + \mathbf{T}_k \cdot \bar{\mathbf{L}}^T - \frac{1}{\tau_{d,k}} (\mathbf{T}_k - \lambda_k^2 \mathbf{I}) - \frac{2}{\tau_{R,k}} \left(\frac{F(\lambda_k) - 1}{\lambda_k} \right) \mathbf{T}_k \quad (2)$$

where $\tau_{R,k}$ and $\tau_{d,k}$ are the Rouse and reptation times associated with the k th mode, $\lambda_k = \sqrt{\frac{1}{3} \text{tr}(\mathbf{T}_k)}$ and $F(\lambda_k)$ is a correction factor accounting for finite chain extensibility¹⁵. The deviatoric conformational stress $\mathbf{S}_{c,k}$ is taken as the deviatoric part of $G_e [\mathbf{T}_k F(\lambda_k) / \lambda_k - \mathbf{I}]$, where G_e is the entanglement modulus. The conformational contribution to the deviatoric stress is thus computed as the sum over all N conformational modes, as $\mathbf{S}_c = \sum_{k=1}^N v_k \mathbf{S}_{c,k}$, where v_k represents the relative volume fraction of the k th Rolie-Poly mode $\left(\sum_{k=1}^N v_k = 1 \right)$.

Model parameters

Rouse and reptation times are referred back to reference values τ^* at a temperature T^* and structural state T_f^* through shift factors a_T and a_{struct} through $\tau_{R,k} = a_T a_{\text{struct}} \tau_{R,k}^*$ and $\tau_{d,k} = a_T a_{\text{struct}} \tau_{d,k}^*$. Glassy relaxation times are referred back to reference temperature, structural state and (unstressed) stress state $\tau_{j,0}^*$ through $\tau_j = a_T a_{\text{struct}} a_{\sigma,j} \tau_{j,0}^*$. Shift factors obey the following equations:

$$\begin{aligned}
a_T &= \exp \left[\frac{\Delta H}{R} \left(\frac{1}{T} - \frac{1}{T^*} \right) \right] \\
a_{\text{struct}} &= \exp \left[\frac{C}{T_f - T_\infty} - \frac{C}{T_f^* - T_\infty} \right] \\
a_{\sigma,j} &= \frac{V_s \tau_{\text{oct},j}^b}{2RT} \frac{\exp \left(-\frac{V_p \sigma_m}{RT} \right)}{\sinh \left(\frac{V_s \tau_{\text{oct},j}^b}{2RT} \right)}
\end{aligned} \tag{3}$$

where $\tau_{\text{oct},j}^b$ is the octahedral shear stress acting on the j th mode, and the rest are material constants:

ΔH is the activation enthalpy, T_∞ is the Vogel temperature, C is the Cohen Turnbull constant, and V_s and V_p are the shear and pressure activation volumes. In the simulations that follow, the values of the constants employed are obtained from Wu and Buckley²⁹ and De Focatiis et al¹⁵. If prediction of the full constitutive response below the glass transition is desired, an evolution equation for fictive temperature with suitable constants can be employed, as suggested previously^{27,32}. In this work, for simplicity, the polymer is assumed to be in equilibrium for temperatures $T \geq 98.9^\circ\text{C}$, and in structural state $T_f = 98.9^\circ\text{C}$ for temperatures $T < 98.9^\circ\text{C}$, consistent with experimentally measured yield stress measurements¹⁵.

The material constants G_e , the entanglement modulus, and M_e and τ_e , the mass and Rouse time of one entanglement length respectively, were identified by treating them as variables for a best fit to the microscopic theory of linear polymer melts of Likhtman and McLeish³³ to linear rheological experimental data on polymers AF and AG¹⁵. The values of the parameters obtained are: $G_e = 317.9 \text{ kPa}$, $M_e = 13.14 \text{ kDa}$ and $\tau_e = 10.57 \text{ s}$ at the reference temperature $T^* = 120^\circ\text{C}$, using the optimiser Reptate³⁴. The finite extensibility material constant λ_{max} was established as 4.09 from an equivalent

Kuhn chain between entanglements¹⁵. The longest mode's (whole molecule) Rouse time and reptation time were computed following Collis et al³⁵ as

$$\begin{aligned}\tau_{R,l}^* &= Z^2 \tau_e \\ \tau_{d,l}^* &= 3 \left(1 - \frac{2.38}{Z^{0.5}} + \frac{4.17}{Z} - \frac{1.55}{Z^{1.5}} \right) Z^3 \tau_e\end{aligned}\tag{4}$$

where $Z = M / M_e$ represents the number of entanglements.

Viscoelastic response and Maxwell modes

Moduli with associated relaxation times for both glassy and conformational modes can be obtained by fitting a discrete spectrum of Maxwell modes to experimental data from viscoelastic experiments, most commonly linear dynamic mechanical analysis (DMA) for glassy modes, and linear melt shear rheology for conformational modes, to cover the range of frequency of interest. In the present authors' original implementation of the constitutive model, the discrete spectrum was fitted to experimental data from two monodisperse linear PS grades¹⁵. This approach required linear melt rheology to be measured experimentally for each grade of polymer, since, for entangled polymers and for sufficiently low reduced frequencies, this is a strong function of the number of entanglements, and hence of molar mass. It is well known, however, that the high frequency part of the spectrum generally obtained from DMA data is insensitive to molar mass for sufficiently entangled polymers (as demonstrated by yield stress measurements on several monodisperse PS grades by Wu and Buckley²⁸). Hence a single set of DMA measurements can normally be considered representative of a given polymer species. In principle, only the response at frequencies $\omega < 1 / \tau_e$ should be dependent of molar mass since this is the part of the spectrum associated with length scales longer than one entanglement, where Rouse times scale with

M^2 and reptation times scale with $M^{3.4}$. In practice, however, this is true only for highly entangled polymers, where the effect of dilution from unentangled ends on relaxation processes is small. From visual observation of experimental rheometric and DMA data on polymers AF and AG, the point at which the response begins to be affected by molar mass was observed to be closer to $\omega \sim 10 \text{ s}^{-1}$ at 120°C^{15} . This compares with $1/\tau_e \approx 0.1 \text{ s}^{-1}$. Thus, in the toolbox only the linear viscoelastic response for $\omega > 10 \text{ s}^{-1}$ was taken to be a material constant, independent of grade of polymer, and employed in the evaluation of Maxwell modes that follows. To aid the reader, the process of identification and partitioning of the Maxwell modes is shown schematically in Figure 4.

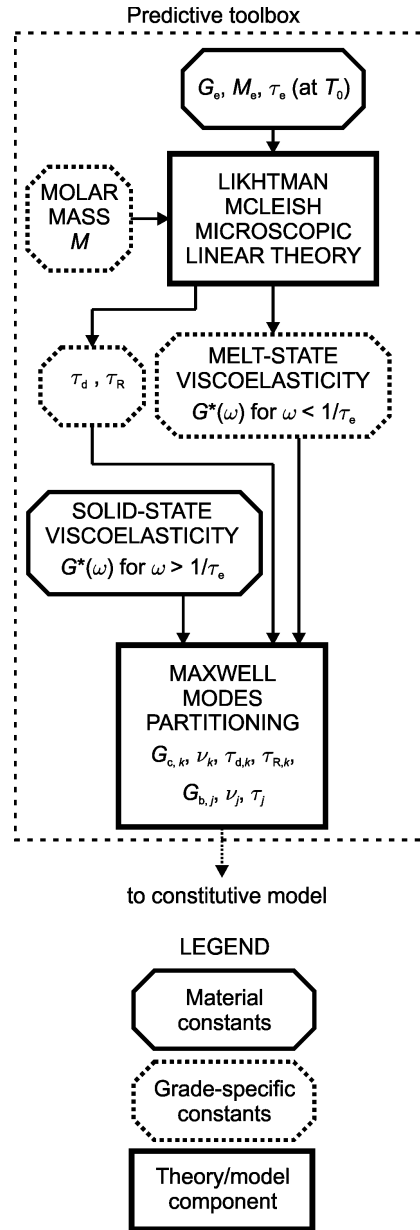


Figure 4 The process of obtaining and partitioning discrete Maxwell modes for the constitutive model with the toolbox, using the Likhtman-McLeish theory to generate the linear rheology based on molar mass.

The linear viscoelastic frequency response can be predicted directly by the quantitative theory of Likhtman and McLeish³³ for a monodisperse polymer of given molar mass, and hence Z , using the

material constants G_e , M_e and τ_e , either by appropriate Fourier transformation of the relaxation function³³, or more conveniently by using the optimiser Reptate³⁴. Figure 5 illustrates theory predictions of the real and imaginary parts of the complex linear viscoelastic modulus for four monodisperse PS grades.

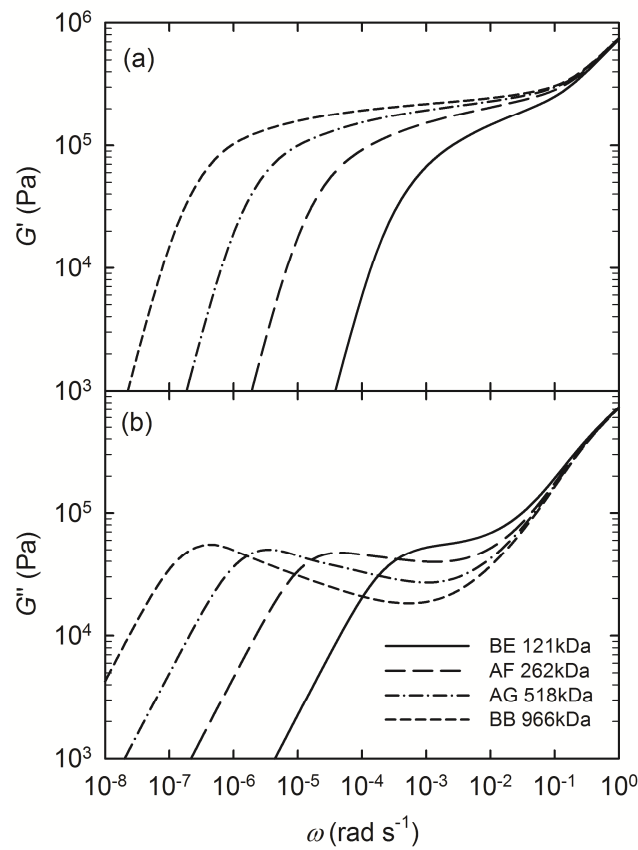


Figure 5 Predictions of the (a) storage modulus and (b) loss modulus of four linear monodisperse PS grades using the Likhtman-McLeish linear theory at a reference temperature of 120 °C.

A discrete relaxation spectrum was then fitted to a combination of the experimental linear viscoelastic data for $\omega > 10 \text{ rad s}^{-1}$, and the linear viscoelastic data from theory predictions for $\omega < 10 \text{ rad s}^{-1}$ (for PS at 120 °C). Starting at the longest relaxation time, $\tau_d = \tau_{d,1}$, one mode was assigned per decade of time

to cover the frequency range of interest, using an in-house optimiser minimising the rms error between the values of $\log G'$ and $\log G''$ as obtained from the combination of experimental DMA data and Likhtman-McLeish theory predictions, and as calculated from

$$G' = \sum_{i=1}^{M+N-1} G_i \frac{\omega^2 (\tau_{d,i})^2}{1 + \omega^2 (\tau_{d,i})^2}, \quad G'' = \sum_{i=1}^{M+N-1} G_i \frac{\omega \tau_{d,i}}{1 + \omega^2 (\tau_{d,i})^2}. \quad (5)$$

where M and N are the number of glassy and Rolie-Poly modes respectively. The condition

$\sum_{k=1}^N G_k = G_e$ was imposed, restricting Rolie-Poly modes to the conformational response.

The linear viscoelastic complex shear moduli computed from the Maxwell modes for materials BE and BB are illustrated in Figure 6. A total of 5 Rolie-Poly modes and 12 glassy modes were required for material BE, and 7 Rolie-Poly modes and 13 glassy modes for material BB. The volume fractions associated with each mode for materials BE and BB are illustrated in Figure 7. Values of $\tau_{R,k}$ are computed from the equivalent values of Z_k corresponding to each Rolie-Poly mode using equation (4)¹⁵.

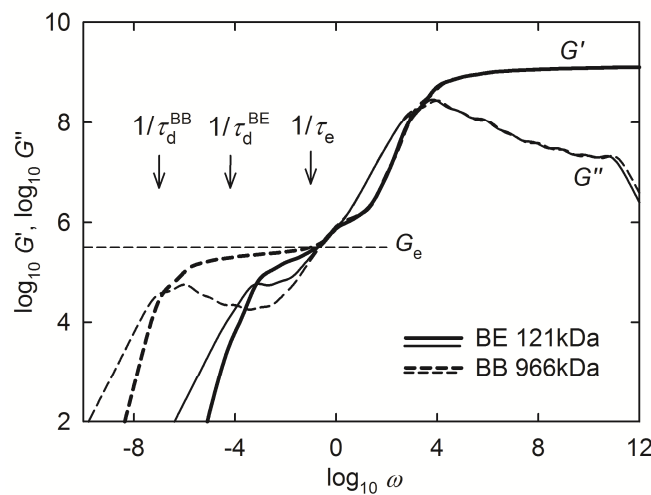


Figure 6 Real and imaginary parts of the linear viscoelastic complex shear moduli of materials BE and BB obtained from the Maxwell modes at a reference temperature of 120 °C. Also shown are the positions of

the whole molecule reptation times for both polymers, the Rouse time of one entanglement length, and the value of the entanglement modulus G_e .

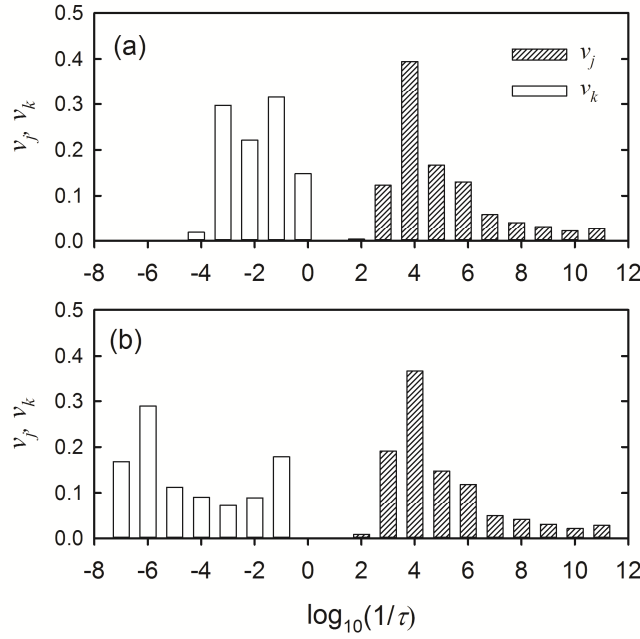


Figure 7 Volume fractions of the fitted discrete relaxation spectra obtained (a) for material BE from 17 Maxwell modes (5 Rolie-Poly and 12 glassy), and (b) for material BB from 20 Maxwell modes (7 Rolie-Poly and 13 glassy).

Process simulations

The toolbox is employed to generate the necessary parameters (the spectra of Maxwell modes) for the constitutive model to simulate the three stages of the process by which orientation is frozen into the specimens. The first stage consists of an isothermal uniaxial orientation through to $\lambda = 3$ at a rate of $\dot{\epsilon} = 0.02 \text{ s}^{-1}$ for a range of temperatures between 105 – 145 °C, during which time the polymer is assumed to be in structural equilibrium. The second stage consists of a fast quench through to 20 °C at fixed deformation, at a rate of 15 °C s⁻¹. When the temperature falls below 98.9 °C, the specimen is

assumed to enter the glassy state, and to remain at a structural state of $T_f = 98.9^\circ\text{C}$ for the remainder of the simulation. This structural state is consistent with experimental measurements of yield stress on polymers AF and AG¹⁵. The third and final stage consists of a fast unloading through to zero net stress at a deformation rate of $\dot{\epsilon} = -1\text{ s}^{-1}$. Thus, the simulation predicts a state of self-stress for unloaded oriented specimens at room temperature, with non-zero bond-stretching and conformational stress tensors $\mathbf{S}_b = -\mathbf{S}_c$.

Prediction of birefringence

In oriented polymers, optical birefringence arises from two independent sources: bond stretching distortions and from conformational alignment of the molecules. Hence, birefringence can be computed as the sum of two independent contributions: one arising from the in-plane principal bond-stretching stress difference ΔS_b and another from the in-plane conformational principal stress difference ΔS_c . In terms of the multimodal constitutive model, this is expressed as

$$\Delta n = \Delta n_b + \Delta n_c = C_b \sum_{j=1}^M v_j \Delta S_{b,j} + C_c \sum_{k=1}^N v_k \Delta S_{c,k} \frac{H(\lambda_k / \lambda_{\max})}{H(1 / \lambda_{\max})} \quad (6)$$

where $H(x) \approx 1 + x^2/3 + x^4/3$ is a correction factor accounting for the non-linear relationship between force and end-to-end distance in chains at large extensions¹⁴, and $C_b = 8.3 \times 10^{-12}\text{ Pa}^{-1}$ ³⁶ and $C_c = -4.5 \times 10^{-9}\text{ Pa}^{-1}$ ³⁷ are the stress-optical coefficients for PS. The reader is advised to consult reference¹⁴ for a more detailed discussion. Computations of birefringence from toolbox simulations are shown in Figure 1. For all orientations and materials explored here, due to the substantial difference in magnitude between the conformational and the bond-stretching stress-optical coefficients the conformational component of birefringence accounts for more than 99.7% of the total birefringence.

Prediction of craze initiation stress

In a previous study of crazing in oriented PS, the present authors demonstrated experimentally that the increase in the stress required for craze formation relative to the isotropic, $\sigma_c - \sigma_c^{\text{iso}}$, is proportional to optical birefringence for a wide range of orientations⁹. The justification for this proportionality is based on Maestrini and Kramer's postulate, that a back-stress acts to increase the stress required for craze formation σ_c relative to the isotropic σ_c^{iso} ⁹. Since for moderate levels of birefringence the conformational birefringence is directly proportional to the conformational deviatoric back stress through a stress-optical coefficient C_c , the relationship can be expressed as

$$\sigma_c - \sigma_c^{\text{iso}} = \Delta S_c / \beta \quad (7)$$

where β is a constant, previously determined by the present authors using birefringence measurements to be 0.059 ± 0.002 for PS¹⁰. Thus, knowledge of the frozen-in conformational stress tensor S_c and of the isotropic craze initiation stress enables predictions of craze initiation stress in uniaxially melt-oriented specimens.

An extensive study of isotropic craze initiation stress performed on 14 monodisperse linear polystyrenes concluded that, for 300 s creep in DEG, and for PS of molar mass of 140 kDa and above, the isotropic craze initiation stress $\sigma_c^{\text{iso}} \approx 16.1 \pm 1.4$ MPa is invariant of molar mass³⁸. This means that for all polymers considered in this study it can be effectively considered as a material constant.

The increase in crazing stress relative to the isotropic is computed from the conformational stress difference obtained from toolbox simulations using the constitutive model for the full range of experimental orientation temperatures, for polymers BE, AF and AG, and is shown in Figure 2.

DISCUSSION

As can be seen in Figure 1, the toolbox is successfully able to account for the role of molar mass on birefringence in oriented PS, and correctly predicts the experimental observation that birefringence increases with molar mass at a given draw temperature. Additionally, the toolbox also accounts for another observation: that the relative effect of molar mass is greatest at the highest draw temperatures, and smallest at the lowest draw temperatures.

The numerical values of birefringence obtained from the toolbox are generally in agreement with the experimental data for the draw temperatures $T \geq 115$ °C. This corresponds to the melt drawing regime for which $Wi_e < 1$; the temperature at which $Wi_e = \dot{\epsilon}\tau_e = 1$ is 115.7 °C, and is marked on Figure 1. The region on the left, where $Wi_e > 1$, represents a drawing regime where sub-entanglement stretch of the molecules is occurring, and toolbox predictions of birefringence are smaller than experimental measurements suggest. This discrepancy is not unexpected, and has been reported previously^{14,15}. The reason for its occurrence is that neither Rolie-Poly modes nor glassy modes take any account of contributions arising from sub-entanglement stretch. In the region on the right, where $Wi_e < 1$, supra-entanglement stretch dominates, and there is good quantitative agreement between predictions and experiment; the average difference between toolbox prediction and experiment is 17%, and is largest at

the smallest birefringence values, where there is greatest experimental uncertainty due to limits on the measurement accuracy of the compensator.

There is a consistent, small overprediction of birefringence for polymer BB, with the highest molar mass. This could be accounted for by a small degree of residual in-plane molecular orientation in the prismatic bars, after moulding and prior to melt-drawing. At the moulding temperature of 170 °C, the reptation time $\tau_d = 645$ s, is of the same order of magnitude as the time for which the polymer was held at temperature after pressing and prior to cooling. An alternative explanation is that the polymer could have experienced a small degree of degradation during moulding, which would lead to a reduction in molar mass, and hence of relaxation times, orientation and birefringence at a given draw temperature. Although the polymer could be moulded at a higher temperature to limit residual orientation, this also increases the likelihood of degradation, and is a common problem with polymers of very high molar mass.

Predictions of craze initiation stress from the toolbox are compared with experiment in Figure 2. The toolbox is successfully able to account for the role of molar mass on craze initiation stress in oriented PS, and correctly predicts increasing crazing stress with molar mass for a given draw temperature. The toolbox predictions also match the experimental observation that the effect of molar mass on craze initiation stress is greatest at intermediate draw temperatures, and smallest at the lowest and highest draw temperatures. At the lowest draw temperatures, relaxation times during melt-drawing are very long, and molecular orientation occurs with little to no relaxation (and hence independently of molar mass). At very high temperatures, there is almost complete relaxation during melt-drawing, and the oriented polymers craze at a similar stress to isotropic polymers of the same molar mass.

Due to the nature and miniaturisation of the crazing experiments, there is more uncertainty on the values obtained from experiment compared with birefringence¹⁰. The numerical values of the predictions are quantitatively in reasonable agreement with the experimental data, with an average difference between toolbox and experiment of 5.8 MPa, or 34% of the matching measured experimental value, across the full range of materials and draw temperatures explored.

Although the constitutive model has to date only been successful in predicting properties of monodisperse linear polymers, the methodology employed in the toolbox is more widely applicable. Through the inclusion of theories for the prediction of the linear and non-linear viscoelastic response of polymers with different architectures (eg. long-chain branched³⁹, dendrimers⁴⁰, or comb polymers) and with different molar mass distribution (eg. bimodal⁴¹ or multimodal), it will be possible to predict solid-state properties of a much wider range of industrially relevant glassy polymers. Research is presently underway at our Nottingham laboratory to extend the toolbox and the experimental validation to bimodal monodisperse linear blends, and to fully polydisperse linear polymers.

CONCLUSIONS

This study has presented a toolbox for the prediction of birefringence and craze initiation stress in oriented monodisperse linear polymers of known molar mass but unknown rheology. The toolbox relies on a previously proposed melt-solid constitutive model to provide the necessary information required to predict both birefringence and craze initiation. The Likhtman-McLeish theory for linear rheology of entangled polymers was employed to generate part of the linear viscoelastic spectrum required by the constitutive model, and all other parameters required (except the molar mass itself) are material

constants. The toolbox was applied to four monodisperse linear grades of polystyrene, for two of which the linear rheology is unknown, in order to generate the molar mass dependent input parameters to the constitutive model. All other parameters were material constants.

Simulations of the process of melt-drawing at a range of temperatures between 105 °C and 145 °C, quenching and unloading were performed using the constitutive model. Outputs were then combined with existing theories to produce predictions of birefringence and of craze initiation stress. These were compared to new experimental measurements of birefringence and of craze initiation on two grades of linear monodisperse polystyrene of substantially different molar mass, and to literature data.

The toolbox predictions were able to account for all observed experimental trends, and in particular for the effect of molar mass on both birefringence and craze initiation. Birefringence predictions were on average within 17% of experimentally measured quantities for all supra-entanglement orientation states and molar masses probed. As sub-entanglement orientation is not presently featured in the underlying theory, the constitutive model is not able to correctly predict orientation, and hence birefringence for processes where $Wi_e > 1$. Crazing predictions were on average within 34% of experimentally measured quantities for the full range of orientations and polymers explored.

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FIGURE CAPTIONS

Figure 1 Experimental measurements of birefringence as a function of draw temperature for specimens of BE and BB drawn at a strain rate of 0.02 s^{-1} to a draw ratio of $\lambda = 3$ and immediately quenched (triangles and diamonds). Also shown are measurements of birefringence on two further grades of monodisperse polystyrene AF and AG oriented under the same conditions from ref. ¹⁴ (circles and squares). Simulations of birefringence performed using the toolbox and constitutive model (lines).

Figure 2 Measurements of the increase in craze initiation stress with orientation as a function of draw temperature for specimens of BE drawn at a strain rate of 0.02 s^{-1} to a draw ratio of $\lambda = 3$ and immediately quenched (triangles). Also shown are measurements of craze initiation stress on two further monodisperse polymers drawn under the same conditions from ref. ¹⁰ (circles, squares). Toolbox predictions of the increase in craze initiation stress with orientation performed using the toolbox and constitutive model (lines).

Figure 3 A schematic outline of the elements, inputs and outputs of the toolbox. The process of obtaining Maxwell modes and partitioning is shown in greater detail in Figure 4.

Figure 4 The process of obtaining and partitioning discrete Maxwell modes for the constitutive model with the toolbox, using the Likhtman-McLeish theory to generate the linear rheology based on molar mass.

Figure 5 Predictions of the (a) storage modulus and (b) loss modulus of four linear monodisperse PS grades using the Likhtman-McLeish linear theory at a reference temperature of 120°C .

Figure 6 Real and imaginary parts of the linear viscoelastic complex shear moduli of materials BE and BB obtained from the Maxwell modes at a reference temperature of 120°C . Also shown are the positions of the whole molecule reptation times for both polymers, the Rouse time of one entanglement length, and the value of the entanglement modulus G_e .

Figure 7 Volume fractions of the fitted discrete relaxation spectra obtained (a) for material BE from 17 Maxwell modes (5 Rolie-Poly and 12 glassy), and (b) for material BB from 20 Maxwell modes (7 Rolie-Poly and 13 glassy).

Table 1 Molar mass measurements obtained by triple detection SEC for polystyrene samples BE and BB used in this study, and for polystyrene samples AF and AG from reference ¹⁵.

GRAPHICAL ABSTRACT

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TITLE

A toolbox for parameter-free predictions of solid-state properties of monodisperse glassy polymers with frozen-in molecular orientation

TEXT

A toolbox that allows designers to predict the properties of oriented glassy polymers using only existing material constants is constructed from a constitutive model applicable to both polymer solids and polymer melts. Two solid-state properties of practical engineering interest are considered: optical birefringence, and craze initiation stress. Predictions from the toolbox are compared to new experimental measurements on well characterized grades of monodisperse polystyrene, and confirm that the toolbox can account for the effect of polymer molecular weight.

GRAPHICAL ABSTRACT FIGURE ((50 mm wide by 50 mm high))

